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Ammonia- hydrogen combustion in a swirl burner with reduction of NO_x emissions

Najlaa Ali Hussein [a, b, *], Agustin Valera-Medina [a], Ali Safa Alsaegh [a,b]

[a] School of Engineering, Cardiff University, Queen's Building, Cardiff CF24 3AA, United Kingdom
[b] University of Babylon, Hillah, Babel, 51003, Iraq

Abstract

Recently, ammonia is being considered for fuelling gas turbines as a new sustainable source. It can undergo thermal cracking producing nitrogen, hydrogen and unburned ammonia, thus enabling the use of these chemicals most efficiently for combustion purposes. Ammonia being carbon-free may allow the transition towards a hydrogen economy. However, one of the main constraints of this fuelling technique is that although the combustion of ammonia produces no CO_2, there is a large NO_x proportion of emissions using this fuel. In this work, cracked ammonia obtained from a modified combustion rig designed at Cardiff University was used to simulate a swirl burner under preheating conditions via heat exchangers. The primary objective of this system is to find new ways for the reduction of NO_x emissions by injecting various amounts of ammonia/hydrogen at different mixtures downstream of the primary flame zone. The amount of injected ammonia/hydrogen mixture (X) taken from the thermal cracking system was ranged from 0%-4% (vol %) of the total available fuel in the system while the remaining gas (1.00-X) was then employed as primary fuel into the burner. CHEMKIN- PRO calculations were conducted by employing a novel chemical reaction code developed at Cardiff University to achieve the goal of this paper. The predictions were performed under low pressure and rich conditions with an equivalence ratio ϕ =1.2 in a swirl burner previously characterised at output powers of ~10 kW. Ammonia and hydrogen blends were evaluated from 50% NH_3 (vol %) with the remaining gas as hydrogen, continuing in steps of 10% (vol %) NH_3 increments. Results showed that the minimum unburned ammonia and higher flame temperature were achieved at 60%-40% NH_3-H_2 when compared to other blends but with high NO emissions. These NO levels were reduced by injecting a small amount of NH_3/H_2 mixture (X=4 %) downstream the primary zone in a generated circulations promoted by the new design of the burner which affecting the residence time hence reducing the NO emission in the exhaust gas.

Keywords: Ammonia/Hydrogen combustion; Nitrogen oxides; Gas turbine

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Nomenclature

a_{stoi}	moles of air for stoichiometry
b,c	coefficients of products in NH_3/H_2/ Air chemical reaction
x,y	coefficients of reactants in NH_3/H_2/ Air chemical reaction
X	volumetric fraction of ammonia/hydrogen that is injected in the post-combustion section
Φ	Fuel-air equivalence ratio

1. Introduction

One of the most significant research discussion is the increase in air pollution and global warming due to greenhouse effects and acid rain, all issues considered very dangerous to public health. Therefore, search for alternatives to fossil fuels has extended in all directions. In recent decades, ammonia has been used as a chemical for hydrogen storage that can be easily dissociated and used as a sustainable fuel for transport fuel cells and power generation. From a technical point of view, NH_3 offers significant advantages in comparison to hydrogen in cost and convenience as a fuel due to its higher density and its easier storage and distribution. Ammonia is easier to produce, handle, store and distribute with an existent, well-developed infrastructure and has promising commercial viability. The hydrogen density of NH_3 is 4 times higher than the demonstrated density of the most advanced methods in metal hydrides [1]. Furthermore, ammonia's cost per volume of stored energy is less expensive than of hydrogen [2-3]. Despite its toxicity, ammonia presents a significantly lower fire hazard compared to hydrogen and gasoline [4-5]. Additionally, ammonia has proven to be a satisfactory substitute for hydrocarbon fuels in a gas turbine engine and showed that high efficiencies with ammonia combustion are possible [6].

Due to its noticeably low flame speed, ammonia is very difficult to use directly in conventional internal combustion engines (ICEs) and gas turbines (GTs). Therefore, ammonia needs to be partially cracked into hydrogen and nitrogen to become an efficient fuel for these devices. Several authors have studied the structure of partially cracked ammonia-air flames [7-8], leading to the development of thermal cracking processes. Furthermore, other researchers [9-10] have documented effective power generation using the cracked molecule via catalytic processes. It is interesting that the literature for thermal cracking is limited. In terms of gas turbines operation, Valera-Medina et al. [11] presented studies using a generic swirl burner that was fueled by a variety of ammonia/methane blends which show a reduction in NO_x and CO emissions at high equivalence ratio > 1.10. Hayakawa et al. [12] studied reaction enhancement and stability of ammonia flames using hydrogen addition, demonstrating that the use of ammonia blends can be potentially used for efficient combustion of NH_3.

Many numerical studies and fundamental experimental investigations have also predicted the variety in ammonia combustion processes. Xiao et al. [13] compared his work with many previous studies [14-16] to identify the best reaction mechanism for the analyses of ammonia/ methane combustion under real gas turbine conditions. Numerous experimental studies of premixed $NH_2/H_2/O2/CH_4$ /Ar flames have also been investigated by [15, 17] at low pressure by using tunable synchrotron vacuum ultraviolet (VUV) photoionisation and molecular beam mass spectrometers (MBMS), finding a great divergence between various blends and their inherent combustion properties. Lee et al. [18] evaluated unstretched laminar burning velocities and stretch effects for laminar, premixed H_2-NH_3-air flames in a freely propagating spherical configuration and compared results with numerical predictions. They found that hydrogen substitution enhanced NO_x and N_2O emissions in fuel -rich ammonia /air flames. Valera-Medina et al. [19] demonstrated that high hydrogen concentration leads to high NO emissions combined with low operability range. Therefore, although hydrogen is an important enhancer of combustion parameters such as flame speed and reactivity, it is clear that further research is needed to employ it in the right concentration in order to avoid an increase in NO.

In the current research, a previously characterized swirl burner [20] was employed. Different to the current system, the novel device uses bluff bodies that can be used to pre-crack thermally ammonia. A diagram of the conceptual design is provided in Fig. 1. The primary objective of this work is to study the potential of using NH_3 as a clean fuel, investigating NH_3/H_2 -air combustion and emissions characteristics under various injection regimes. Various blends were analyzed in order to recognize the one that will produce the lowest NO with the highest combustion efficiency (i.e. lowest unburned ammonia and higher temperatures). Moreover, understanding the

effects of NH_3 on NO emissions at various concentrations were also pursued through this research. Finally, the effect of the post-combustion injection of ammonia/hydrogen for different blends and effect of residence time was also studied in order to enable the further reduction of any remaining NO emission.

2. Numerical Methods

2.1. Combustion characteristics at low-pressure rich conditions

The initial composition of the fuel mixture is calculated using an equivalence ratio ϕ =1.2 with power outputs ~10 kW, inlet temperature of 657K, and using a great variety of blends as listed in Table 1. As illustrated in Table 1, 5 NH_3/H_2 blends were evaluated from 50% NH3 (vol%) with the remaining as hydrogen and continuing in steps of 10% (vol%) NH_3 increments. The overall complete chemical reaction used in the calculations is presented in Eq. (1).

$$xNH_3 + yH_2 + a_{stoi.}\,(O_2 + 3.76N_2) \rightarrow b\,H_2O + cN_2 \quad (1)$$

In the simulations, an adiabatic condition was assumed, as heat losses in the current system at the low power rates assumed were considered negligible [21]. For laminar flame studies, a freely propagating premixed flame in rich NH_3/ H_2/ air mixture at 3 bar was simulated for different amounts of injected ammonia/hydrogen ratios (X), which were changed from 0% to 4% (vol%).

2.2. Chemical-Kinetic

CHEMKIN- PRO calculations were conducted employing a novel reaction model developed at Cardiff University based on Mathieu's mechanism [22]. The simulation was conducted using both a laminar Flame Speed calculator and a Chemical Reactor Network (CRN) model that included four clusters formed by two-hybrid Perfectly Stirred Reactor-Plug Flow Reactor (PSR-PFR) configurations. This type of network is commonly used to simulate mixing and flow characteristics in gas turbine combustors [23]. A schematic of the network is presented in Fig.2. The first cluster represents the swirling flame with a central recirculation zone (CRZ). The second cluster represents the injected mass flow of X at the specific NH_3/H_2 blend towards the post-combustion zone to reduce NO levels through a second recirculation zone, finally ending in a 15 cm duct. Different post-combustion recirculation zones were assessed to evaluate the impact of various bluff body configurations.

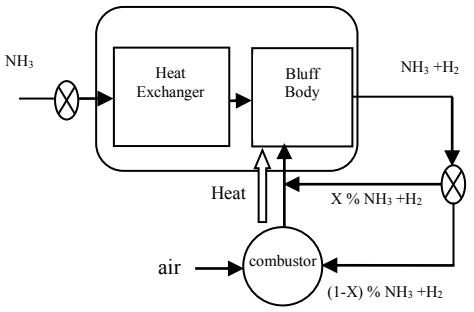


Fig. 1. A conceptual diagram of the system

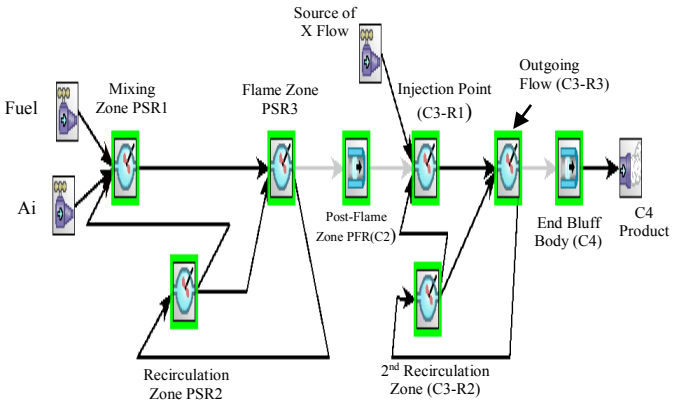


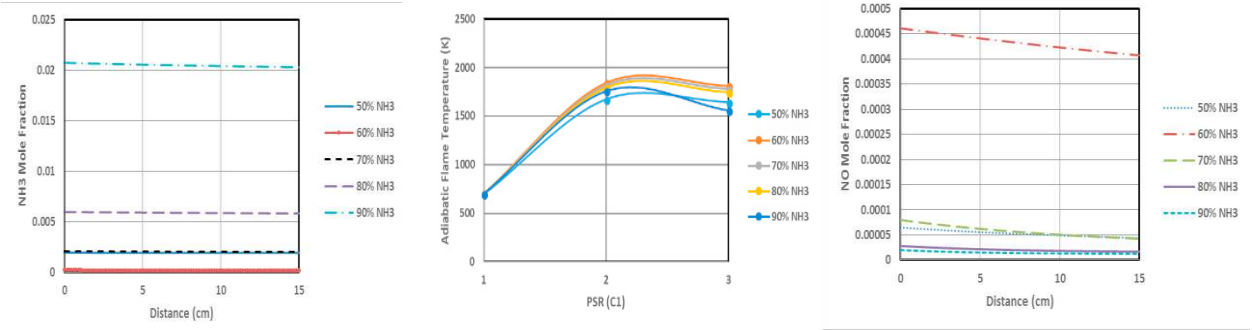
Fig. 2. PSR-PFR Schematic for ammonia cycle

Table 1. Numerical matrix of initial fuel/air mixture with ϕ =1.2, power ~10 kW

NH_3%	NH_3 (mol/s)	H_2 (mol/s)	Mass NH_3 (g/s)	Mass H2 (g/s)	Mass of Air (g/s)
50	0.017973	0.017973	0.305541	0.035946	2.158916773
60	0.020993702	0.013995801	0.356892932	0.027991602	2.601819455
70	0.02385821	0.01022495	0.40558957	0.0204499	2.631858826
80	0.02657807	0.00664452	0.45182719	0.01328904	2.660464836
90	0.02916397	0.00324044	0.49578749	0.00648088	2.687621306

3. Results and Discussion

To evaluate the best ammonia and hydrogen blends which are used in this study, numerical simulations were undertaken for 5 NH_3/H_2 blends depending on highest combustion efficiency. Figure 3 indicates that the lowest amount of unburned ammonia occurs at 60%NH_3-40%H_2 compared to other blends with highest flame temperature. As a result, a 60% NH_3 ammonia fraction has been selected as the best case regarding the unburned ammonia but with highest NO level as shown in figure 3 (c) as they cannot reduce together in the same time. Accordingly, to minimise the NO formation, a small amount of ammonia/hydrogen fraction (X) from the total available fuel in the system will be injected downstream the primary flame zone in a high circulation zone.



(a) (b) (c)

Fig. 3. (a) unburned ammonia, (b) Adiabatic Flame temperature (c) NO emissions at different NH_3/H_2 mixture without injection X fuel

Figure 4 shows a comparison of 60%-40% NH_3/H_2 mixtures at X=0-4%, which show the NO formation levels decreasing when increasing X ratio. Furthermore, it can be noticed that the NO levels changes with increasing the residence time in second recirculation zone. It was obvious that NO mole fraction in exhaust gas decrease with increase the residence time. This behaviour indicates that adding NH_3/ H_2 blends as a reducing agent plays a role in consuming NO formed in the post-combustion zone, as expected. Partially cracked NH_2 radicals obtained from the decomposition of hot, injected ammonia will lead to their recombination with NO at lower temperatures, thus following the path $NH_2 \rightarrow NH \rightarrow N_2$. The increment of NH_2 reactions will block those produced by OH emissions, i.e. as the OH radical has been already depleted from the post-combustion zone while consuming NO_x [11]. Figure 5 shows the sensitivity analysis for NO, which identifies the importance of the reaction close to the flame zone. $NH_2+N \leftrightarrow N_2+2H$ is the most promoting reaction for NO formation while reaction $N+NO \leftrightarrow N_2+O$ and $NH_2+NO \leftrightarrow N_2+H_2O$ play an essential role for NO consumption. Figure 6 shows the main reaction pathways of NO formation. The major source of NO formation comes from the oxidation of HNO and NH_2 at high temperatures. However, as previously mentioned, NH_2 at lower temperatures of reaction, i.e. similar to those found in the post-combustion injection, follow a path that leads to N_2 production.

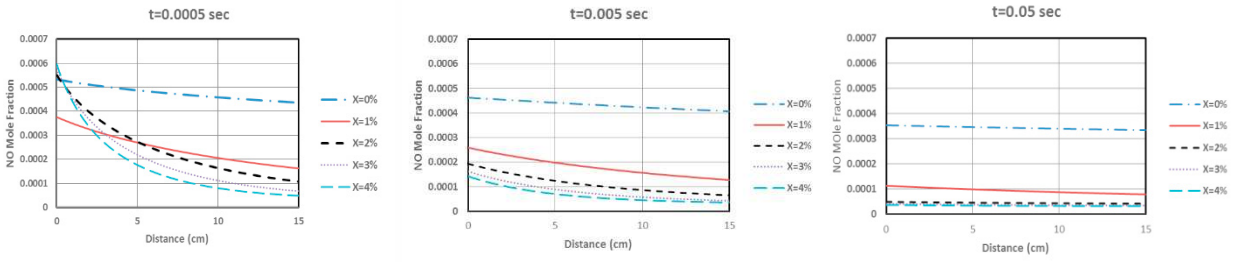


Fig. 4. NO emissions at 60% NH_3/ for X values at different residence time.

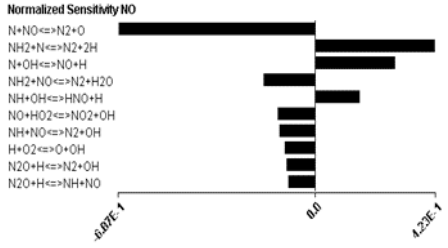


Fig. 5. NO sensitivity in flame zone

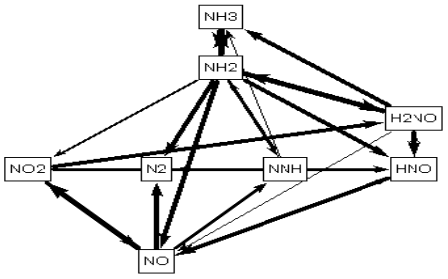


Fig. 6. Ammonia reaction pathway of NO formation in the flame zone

Fig.7. (a) indicate 1-D numerical simulations for the best case was chosen (60% NH_3-40%H_2) at X=4% and residence time=0.05 sec. It shows that the gas ignition occurs in the flame zone (PSR3) with an increase of temperature in the recirculation zone (PSR2) where NH_3 and H_2 keep reacting. It is also noted the increased concentration of water vapour at the hot boundary; this causes a corresponding increase of the flame temperature which caused increased concentration of light radicals such as H_2, OH, O_2 and NO, in the reaction zone. NO_2 is negligible as compared with NO. Figure 7 (b) indicate a rise in temperature because of the reaction of OH, NH_2, NO, OH radicals that are a highly active species at the beginning of the post-flame region reaction with hot H_2. Figure 7 (c,d) indicate the effect of injection strategy of X values from NH_3/ H_2 blends on the amount of uncracked ammonia and NO levels in both post-combustion zone and end of the bluff body respectively.

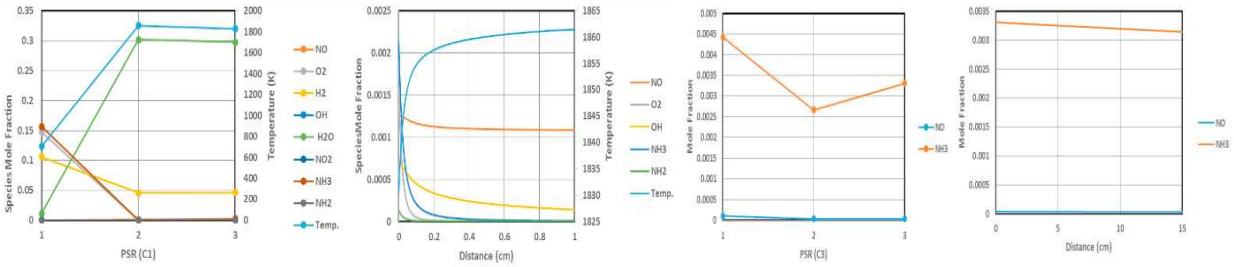


Fig. 7. 1-D Simulation in the (PSR-PFR) reactions using a swirling network for 60% NH_3, X=4% and t=0.05 sec.

4. Conclusion

The design of the burner can affect the flame topology and hence the emission levels. A new thermal cracking system has been designed at Cardiff University to prepare the required fuel for the burning process and promote the flow field characteristics downstream of the primary flame zone and hence drop down the emissions. In this paper, the combustion characteristics of NH_3/H_2/air mixture at low pressure and under rich conditions are examined

numerically. It was recognised that the injecting NH_3 and H_2 downstream the primary flame zone plays a significant role in decreasing the NO_x levels in post flame zone. An injection strategy of different NH3-H2 fractions (X) in the flame shows a promising result for further burners design and study that minimise the combustion process impact on the environment. The minimum NO values were achieved at 60%-40% NH_3-H_2 and X=4%. Also, the increasing of residence time for the second generated recirculation zone tends to enhance NO level to a minimum value. Thus, this injection technique shows a hopeful result for further investigations. This piece of work will be extended to experimental campaign in the next few months to prepare the required data for validation.

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